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Mineralogical Characterization of the Shelburne Marble and the Salem Limestone—Test Stones Used to Study the Effects of Acid Rain

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Mineralogical Characterization of the Shelburne Marble and the Salem Limestone—Test Stones Used to Study the Effects of Acid Rain

By Elaine S. McGee

Shelburne Marble and Salem Limestone samples selected for exposure studies are compositionally homogeneous and are representative of marbles and limestones used in buildings and monuments

U.S. GEOLOGICAL SURVEY BULLETIN 1889

DEPARTMENT OF THE INTERIOR
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U.S. GEOLOGICAL SURVEY
Dallas L. Peck, Director

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Mineralogical Characterization of the Shelburne Marble and the Salem Limestone—Test Stones Used to Study the Effects of Acid Rain

By Elaine S. McGee

Abstract

The Shelburne Marble and the Salem Limestone have been used extensively in buildings and monuments, and for this reason they were selected as test stones for the National Acid Precipitation Assessment Program stone exposure studies. Mineralogical characterization of fresh Shelburne Marble and fresh Salem Limestone provides a basis for recognizing mineralogical changes that may occur in samples when they are weathered.

The Royal variety of Shelburne Marble is a white marble that has gray streaks of inclusions. It is composed predominantly of calcite (97 percent) but contains inclusions of dolomite, layer silicates, framework silicates, and nonsilicates. The inclusions are heterogeneously distributed in the rock and commonly form linear clusters that are dominated by dolomite + phlogopite ± rutile ± chlorite. Less abundant inclusions are muscovite, talc, quartz, feldspar, pyrite, and apatite. All of the minerals that constitute the Shelburne Marble have nearly end-member compositions. Mineral composition, grain size, and inclusion associations may significantly contribute to the durability (or weakness) of marble used in buildings or monuments that are exposed to acid precipitation.

The select buff Salem Limestone is a beige-colored, homogeneous, fossiliferous limestone. It is composed of nearly equal amounts of echinoderm and bryozoan fragments, cemented by calcite with fragments and whole specimens of *Endothyra*, ostracods, gastropods, brachiopods, and pellets. The average fossil size ranges from 0.2 to 0.5 millimeter, but in some areas, the average size is 0.7 millimeter. Fossil constituents such as fenestrate bryozoans (as large as 3.7×2.3 millimeters), echinoderm columnals (diameters from 0.3 to 1.4 millimeters), and ostracods (up to 1 millimeter) are noticeable in some areas because of their large size or unusual shape. The fossils are composed of calcite that does not differ much in composition from the matrix calcite. In the fossils, the average CaO is 55.14 percent, and in the matrix calcite, the average CaO is 55.27 percent. Both the fossils and the matrix contain small amounts of MgO (~0.55 percent). There is no significant compositional difference between the various types of fossils. Very minor quartz and hematite are present as small inclusions in some fossil fragments, particularly in echinoderm columnals, bryozoan stem pieces, and gastropods. The fossil fragments have a pitted surface in polished section, compared with the matrix calcite, that may be caused by very small inclusions that make the fossil fragments more resistant to polishing (and possibly resistant to weathering) than the calcite cement.

The Shelburne Marble and Salem Limestone are typical of marbles and limestones that have been used in many buildings and monuments. The baseline characteristics determined for these stones show that the samples used in this study are representative of these types of building stones, and thus they are appropriate materials to use to study the effects of acid rain on marbles and limestones.

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INTRODUCTION

Stone deteriorates (or weathers) when it is exposed to rain, wind, freezing and thawing, and so on, and although weathering is a natural process, increasing air pollution may be accelerating normal weathering processes. Acid precipitation, formed for the most part from the reaction of sulfur oxides and nitrogen oxides with various oxidizing agents, has been recognized as a widespread environmental problem (Likens and others, 1979; Babich and others, 1980; Armbruster and others, 1983; Franks, 1983). The marked deterioration of some stone buildings, monuments, and statues has been attributed to the effects of acid rain (Pearce, 1985; Peterson, 1985). For example, Skoulikidis (1982) suggested that the degradation of the Acropolis has accelerated over the last 20 to 25 years, coincident with increased industrialization and the use of high sulfur fuels. Concern about this rapid deterioration has prompted many studies that have attempted to determine the extent and causes of damage (Esbert and others, 1981; Guidobaldi, 1981; Butlin and others, 1985; Lal, 1985) and that seek ways of preserving or protecting stone that is particularly susceptible (Gauri, 1978; Accardo and others, 1981; Castro, 1981; Skoulikidis and Beloyannis, 1981).

In the United States, the National Acid Precipitation Assessment Program (NAPAP) is funding studies that address the problem of the effects of acid deposition on stone. Prior studies have been confined to either laboratory experiments or to observations and comparisons of buildings over a period of years. Although both approaches provide useful information, they also have limitations. Laboratory studies provide a controlled situation for the observation and manipulation of reactants but are limited by time constraints and by the difficulty of exactly duplicating the mixture of pollutants and conditions in the urban environment. Surveys of buildings and retrospective examination of photographs to study deterioration lack specific information about the pollution conditions affecting the stone and may lack information about the initial characteristics of the stone. We are conducting an exposed stone study under the auspices of the NAPAP (Task Group VII, Effects on Materials and Cultural Resources) that combines features of both laboratory and retrospective studies of stone weathering. In this study, dimension (building) stone samples have been placed at five exposure sites in the Eastern United States where atmospheric and environmental conditions are carefully monitored (National Acid Precipitation Assessment Program, 1984; Sherwood and Doe, 1984). The stone samples are studied on a yearly or quarterly basis to relate changes in the stones to the monitored atmospheric and environmental conditions (for example, Ross and others, 1989).

Granite, limestone, sandstone, and marble are some of the more commonly used stones in buildings and monuments. For this study, two factors were important in selecting the stone to be tested. The test stone must be representative of the stone that has been used in buildings and monuments and may be at risk from acid deposition effects, and it must show some deterioration effects within the 10-year time constraints of the study. Carbonate stone will show weathering effects more rapidly than granite, which is composed primarily of silicate minerals (Winkler, 1973). Therefore, although granite is the most widely used dimension stone in buildings, monuments, and bridges, we limited our choices of potential test stone to limestone, marble, and carbonate-cemented sandstone. Limestone is the second most widely used dimension stone (Sherwood and Doe, 1984). Marble is less commonly used as a building stone than limestone, granite, and sandstone, but it has been used in many monuments and buildings of historical or cultural value. Although carbonate sandstone is very susceptible to weathering, representative material is difficult to locate because, when sandstone was used in buildings, mostly local sources of sandstone were used. Thus, two stone types, limestone and marble, were selected for the exposure studies. The Salem Limestone from Indiana and the Shelburne Marble from Vermont have been used in many buildings, and both were available from active quarries that also provided stone for a number of buildings built over the past few decades in the Eastern and Midwestern United States. Because the Salem Limestone provided 53 percent of the total limestone dimension stone used in the United States between 1880 and 1980 (D'Agostino and Atelsek, 1984, unpub. U.S. Geological Survey administrative report), it was selected as the limestone test sample (Ross and Knab, 1984). The Shelburne Marble was selected as the marble test stone (Ross, 1985), because, although Georgia and Vermont have produced comparable dollar amounts of marble for use in buildings, the Shelburne Marble from Vermont has been used in the Northeastern United States, the region where acid rain is more of a concern.

Samples of the unexposed limestone and marble must be carefully characterized so that changes in the stone after exposure can be identified. This paper provides the initial mineralogical characterization of the marble and limestone used in the exposure program. The parent mineral phases that are in a rock reflect the environment and chemistry around the stone during lithification, and new phases may be produced in a significantly different environment during weathering. The phases behave in an ordered, predictable way based on their chemical composition and thermodynamic stabilities. Thus, the composition, arrangement, and kinds of minerals that compose the stone will influence how it responds to the environment; it is these features that are the focus of this report.

THE EXPERIMENT

Four sites in the Eastern United States (Newcomb, N.Y.; Chester, N.J.; Washington, D.C.; and Research Triangle Park, N.C.) were initially selected for the stone exposure studies, and 2 years later a fifth site (Steubenville, Ohio) was added. Sites were selected, in part, on the basis of the type of environmental monitoring equipment already present, the geographic location, the average yearly SO_2 levels, and the availability of space for the sample racks. The sites are part of the NAPAP weather and pollution monitoring network, and in addition to the stone samples discussed here, the sites are used for exposure studies of metals and exterior paints. Air quality, meteorology, and rain chemistry parameters are monitored at each site and recorded in a standard computer format used by the Environmental Protection Agency. Some of the conditions that are monitored are atmospheric gas concentration, rain amount and chemistry, particulate amount and chemistry, relative humidity, temperature, and wind speed and direction. A full description of the sites and the types of environmental monitoring employed at the sites is given by Sherwood and Doe (1984), Flinn and others (1985), and Reddy and others (1986). Studies of the stone samples placed at these sites are being conducted by a group of researchers, who are employing a range of techniques. The

Figure 1A. Block of Salem Limestone at the quarry before cutting. Dimensions are 3½×4×9 ft.

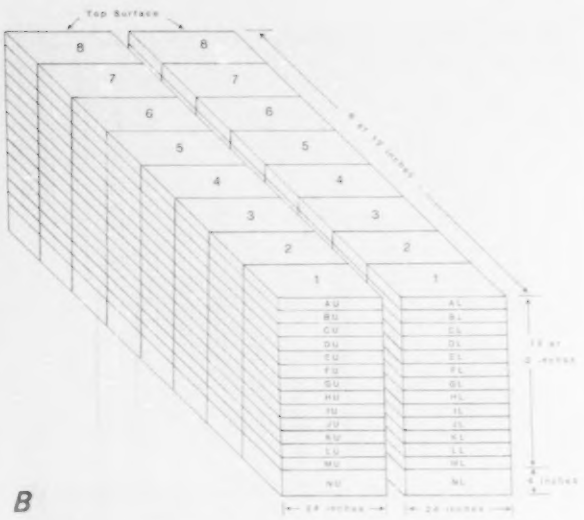


Figure 1B. Diagram of the block, showing labeling of the slabs. U, upper; L, lower.

studies include observations and measurements of changes in mineralogy, chemistry, surface roughness, and the runoff chemistry of the rainwater (Sherwood, 1984).

Two large blocks of limestone and marble (figs. 1*A* and 2*A*, respectively) were obtained for the exposure study from active quarries that have provided stone for many major buildings. A block of Salem Limestone, 3½×4×9 ft, was obtained from the Independent quarry near Bloomington, Ind., and a block of Shelburne Marble, 3½×6½×6½ ft, was obtained from the Danby quarry near Danby, Vt. The selection and procurement of the blocks are described by Ross and Knab (1984) and Ross (1985). Both blocks were cut into 12- × 24-inch slabs at mills near the quarries (Ross and Knab, 1984; Ross, 1985), and the slabs were numbered as shown in figures 1*B* and 2*B*. Most of the studies are being conducted on 2-inch-thick slabs or on briquettes cut from the slabs, but some of the limestone and marble slabs were cut 4 inches thick for some of the specialized tests that required thickness greater than 2 inches (Ross and Knab, 1984). In all, 208 2-inch-thick slabs of limestone and 252 2-inch-thick slabs of marble were made (figs. 1*B* and 2*B*). The 2-inch-thick slabs were finished on one 12- × 24-inch face so that the surface would resemble the surface commonly used for the stone in buildings; the saw cut on the opposite face was not finished. Thus, the limestone samples have a smooth planar finish on the top surface, and the marble samples have an 80 grit finish on the top surface. Some slabs were used for the rainwater runoff studies at the test sites. Other slabs were cut into briquettes that measure 3×3⅜×2 inches (marble) or 2 15/16×3¼×2 inches (limestone) and used in mineralogy, chemistry, and surface roughness studies.

Slabs to be used for the runoff study and for the briquettes were selected to represent the average stone. Because the limestone is fairly homogeneous in overall appearance, slabs were selected from the middle of the block (layers G, H, and I; fig. 1*B*); the specific slabs

Figure 2A. Block of Shelburne Marble at the quarry before cutting. Dimensions are 3½×6½×6½ ft.

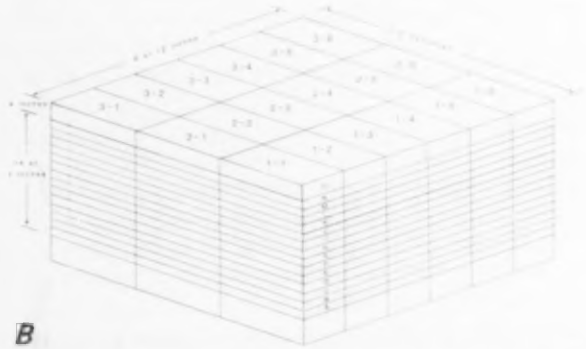


Figure 2B. Diagram of the block, showing labeling of the slabs.

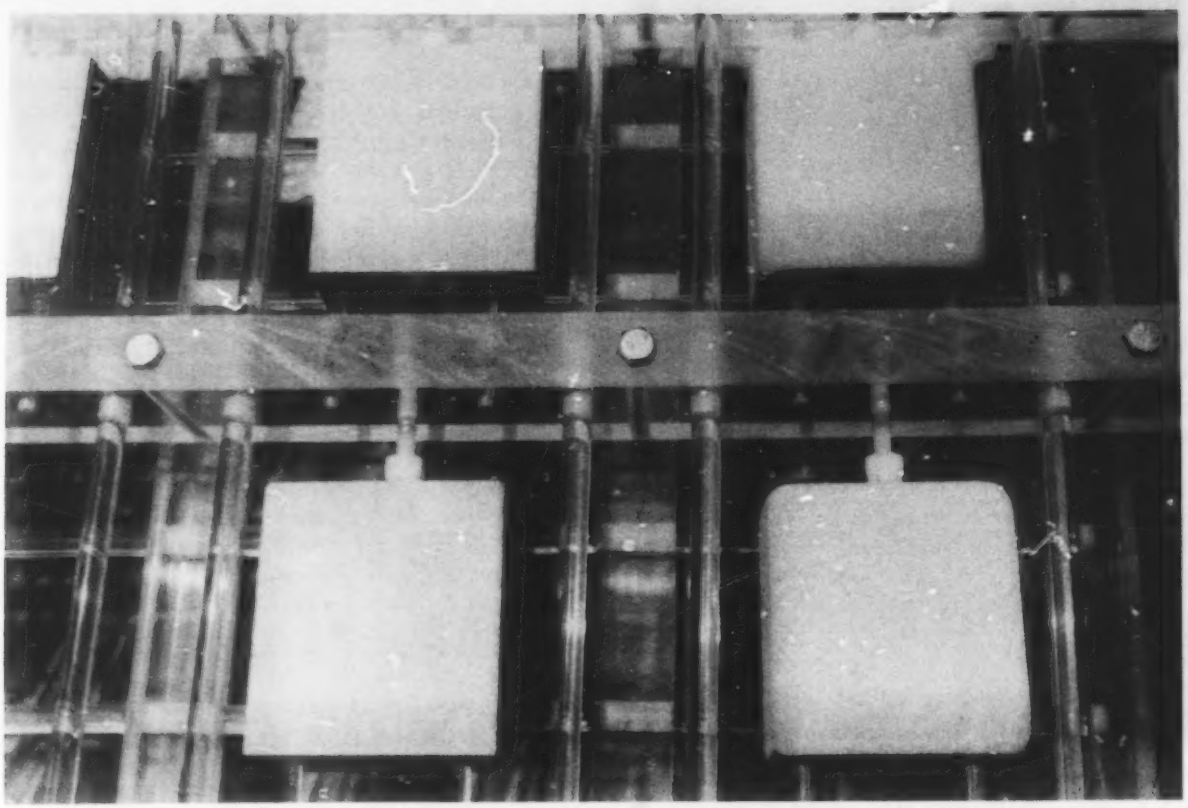


Figure 3. Salem Limestone briquettes in sample rack. Briquettes are approximately 3 inches wide. Note that each briquette is held in place by one screw at the top edge and two dowels at the bottom edge; the bottom surface of the briquette rests on two plexiglass rails. The briquettes on the left of the photograph are used for mineralogy studies; the two briquettes on the right that have rounded corners are used in weight loss experiments.

designated for the mineralogical studies are GL5, HL5, and IL5. The marble is less homogeneous in appearance, and so slabs were selected that contained few of the dark inclusion streaks. The mineralogy samples were made from the H14, E26, C16, G36, N15, and A33 slabs (fig. 2*B*).

The briquettes are held in polymethyl metacrylate (plexiglass) open racks and rest on plexiglass rods that touch the lower surface in only two places (fig. 3). The racks hold 72 samples, and they are arranged side by side in the same relative position at all the sites (from left to right, limestone briquette rack, marble briquette rack, runoff slabs; fig. 4). The samples are positioned so that they face south and are tilted so that the upper surface is at a 30° angle from the horizontal. This arrangement was used for stability and to conform with the ASTM standard for test materials. The briquettes thus provide two analogies to surfaces on buildings. The upper surfaces of the briquettes are boldly exposed and represent those parts of buildings that may be washed by precipitation and thus are exposed to all wet and dry deposition. The lower surfaces of the briquettes are sheltered from direct rainfall and thus represent areas that are not directly washed by precipitation but may experience both dry deposition and dripping or collection of rainwater.

Samples for all studies were installed at the sites on the following dates—North Carolina–May 25, 1984; New Jersey–June 5, 1984; New York–June 19, 1984; Washington, D.C.–August 11, 1984; and Ohio–July 17, 1986. The mineralogy samples are withdrawn at yearly intervals for examination and study. Briquettes used for the mineralogy studies were selected randomly, and the position for each sample in the rack was also determined randomly (National Park Service and Argonne National Laboratory, 1988). To minimize variation among the samples because of exposure position, the limestone and marble samples for a specified year occupy the same slot in their respective racks. For example, the first-year limestone sample is in slot 142, and the first-year marble sample is in slot 242; the first digit of the slot number indicates the limestone and marble rack, respectively. In addition, the samples for a specified year are in the same slot position at all five sites. Table 1 lists the sample numbers of the mineralogy briquettes at each of the sites, by year of withdrawal. The mineralogy samples are

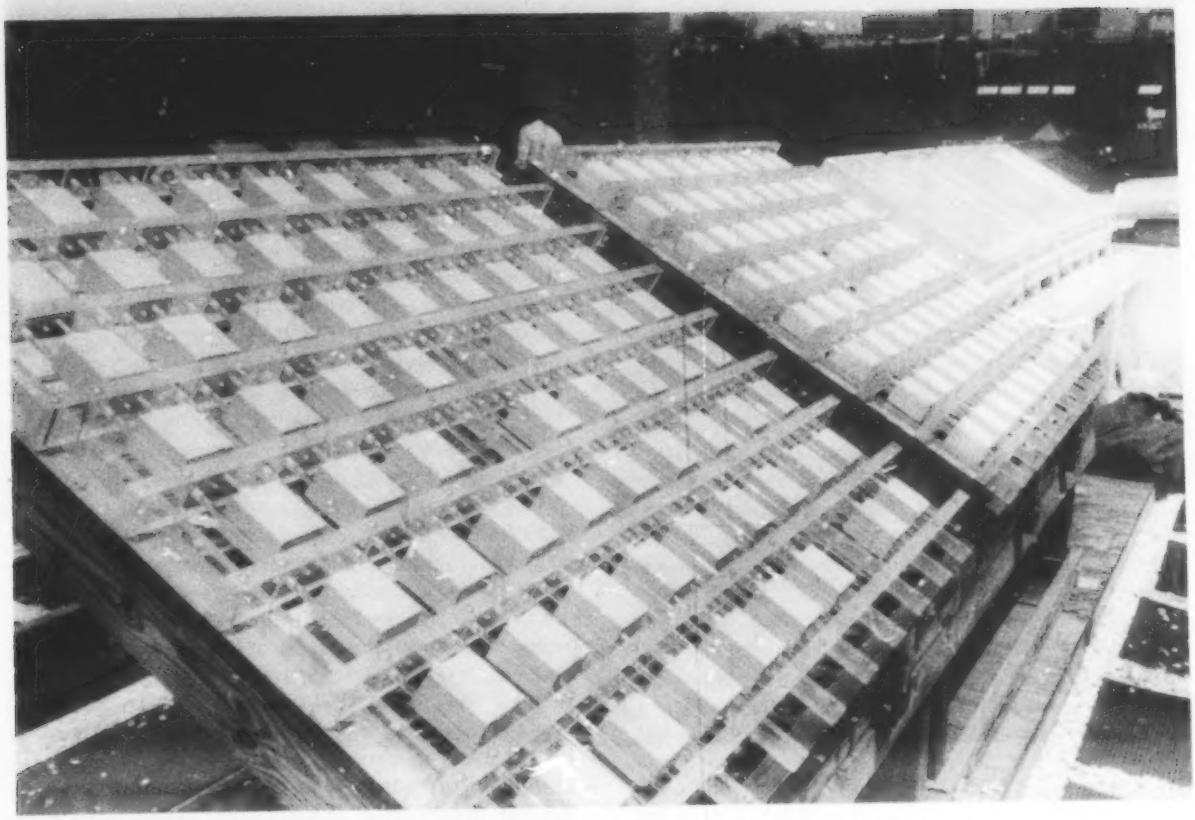
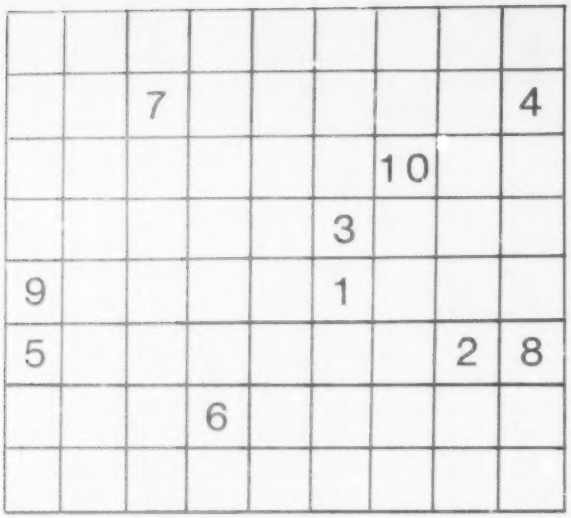


Figure 4. Briquette sample racks at the Washington, D.C., site. Salem Limestone briquettes are in the foreground, Shelburne Marble briquettes are in the center, and the slabs used for runoff experiments are in the upper right of the photograph. The racks are slanted at 30° to the horizontal and face south.

Table 1. Sample numbers, slot numbers, and year of withdrawal of briquettes of the Salem Limestone and Shelburne Marble used for mineralogy studies

Slot no.	Year 1 142	Year 2 153	Year 3 133	Year 4 118	Year 5 146	Year 6 158	Year 7 112	Year 8 154	Year 9 137	Year 10 125
Site					Salem Limestone					
N.Y.	HL5–10	IL5–02	GL5–18	HL5–15	IL5–07	GL5–23	HL5–03	IL5–18	GL5–09	HL5–08
N.J.	HL5–06	IL5–23	GL5–14	HL5–11	IL5–03	GL5–19	HL5–24	IL5–14	GL5–06	HL5–21
D.C.	HL5–14	IL5–06	GL5–22	HL5–19	IL5–11	GL5–03	HL5–07	IL5–22	GL5–16	HL5–17
N.C.	HL5–02	IL5–19	GL5–10	HL5–05	IL5–24	GL5–15	HL5–20	IL5–10	GL5–02	HL5–16
Ohio[1]	IL8–17	HL2–07	GL3–01	HL2–15						
Slot no.	Year 1 242	Year 2 253	Year 3 233	Year 4 218	Year 5 246	Year 6 258	Year 7 212	Year 8 254	Year 9 237	Year 10 225
Site					Shelburne Marble					
N.Y.	G36–20	N15–02	C16–23	N15–09	A33–10	C16–22	N15–15	A33–18	C16–18	N15–18
N.J.	G36–16	N15–23	C16–04	N15–06	A33–01	C16–20	N15–11	A33–23	C16–08	N15–22
D.C.	G36–18	N15–14	C16–19	N15–12	A33–02	C16–06	N15–21	A33–07	C16–14	N15–19
N.C.	H14–22	E26–19	C16–10	H14–14	E26–20	C16–12	H14–05	E26–04	C16–16	H14–06
Ohio[1]	G34–23	K13–17	G22–09	G24–11						

[1]Only four samples were put out at the Ohio site because this site was installed later than the other four, and the experiments were scheduled to end in 1990.



Year	Slot no.	Year	Slot no.
1	142	6	158
2	153	7	112
3	133	8	154
4	118	9	137
5	146	10	125

Figure 5. Briquette rack showing the positions of the mineralogy briquettes by year of withdrawal. Samples were installed at New York, New Jersey, Washington, D.C., and North Carolina in 1984, and so year 1 withdrawals at these sites were made in 1985. Positions were determined by a random process; Shelburne Marble and Salem Limestone briquettes occupy the same position in their respective racks. Limestone briquette slots are numbered 101–172; marble briquette slots are numbered 201–272.

removed on the installation anniversary from predetermined random locations (fig. 5).

The ultimate goal of the mineralogical studies in the exposure program is to look for changes in the mineralogy of the stone and to determine whether those changes are due to the environmental conditions at the exposure sites. Thus, two questions have guided this study of the mineralogy of the unexposed stone: What are the reactants, and what characteristics or features of the minerals may be significant to the weathering of the stone? Knowledge of the stone's mineralogical characteristics and geologic history and studies of stone durability done by others provide some indication of the types of changes that may occur when the stone is exposed in a polluted environment.

SELECTION OF THE STUDY STONE

Shelburne Marble

The Shelburne Marble, quarried in western Vermont and known by the trade name of Vermont marble, was selected as a test stone because it has been used in many monuments and historic buildings (table 2), particularly in the Eastern and Northeastern United States, where acid rain has long been recognized as a problem. The quarry that supplied the stone for the exposure study also supplied stone for the Jefferson Memorial, the Rayburn Building, and the French Embassy in Washington, D.C. (table 2).

Shelburne Marble forms layers that contain different kinds and amounts of inclusions. The inclusions give the marble distinctive colors and striking patterns and may vary significantly from one layer to the next. Six broad groups of colors and patterns identified by Bain (1933) (white with gray dolomite mottling, white, white with greenish veining, gray and blue gray, fine textured black, and red) reflect some of the differences in the layers and illustrate the diverse appearance of the Shelburne Marble. The appearance of the stone and the types of inclusions that it contains influence the uses to which a specific marble can be applied. Thus, the marble-producing companies have given commercial or trade names (for example, Royal, Imperial, Danby, and Dorset B) to marble layers within the Shelburne Marble; the names relate to the color characteristics of the marble. Many names have been used for the various layers. Although the names given to the marbles were used for many years, new names were sometimes given if a quarry changed hands; these name changes make tracing the usage of specific marbles difficult. The Royal marble from the Danby quarry was selected for the exposure study

Table 2. Notable buildings constructed of Vermont marble

[—, date unknown]

Building	Location	Date built
The New York City Library	New York City	1911
The Federal Reserve Bank	Philadelphia, Pa.	—
Buildings of the Harvard Medical School.	Boston, Mass.	~1912
The John Hay Memorial Library.	Providence, R.I.	~1912
Memorial Continental Hall (Daughters of the American Revolution).	Washington, D.C.	1909
The Red Cross Building	do.	1917
The Supreme Court	do.	1936
The Jefferson Memorial	do.	1943
The Rayburn Building	do.	1965
The French Embassy	do.	1984
The Art Association Building	Montreal, Canada	~1912

Table 3. Notable buildings constructed of Indiana limestone

[—, date unknown]

Building	Location	Date built
The Empire State Building	New York City	1931
Rockefeller Center.....	do.	1931
The Metropolitan Museum of Art.	do.	—
The National Archives	Washington, D.C.	1938
The Pentagon	do.	1941
The Department of Interior	do.	1937
The National Cathedral.....	do.	1907 (started)
The Indiana Capitol Building ..	Indianapolis, Ind.	1878
The University of Chicago	Chicago, Ill.	~1890
The Academy of Science.....	do.	~1890

because it is similar in appearance and physical characteristics to the marble used in many of the buildings listed in table 2 (Ross, 1985).

Salem Limestone

The Salem Limestone, known by the trade name of Indiana limestone, has been used extensively in the construction of government and private buildings in the Eastern and Midwestern United States. Prior to the appearance of portland cement around 1900, limestone was the cheapest durable building material that was homogeneous in color and texture (Rooney, 1970). The dimension (building) stone facies of the Salem is uniformly textured, is a good freestone (meaning that it can be easily carved in any direction), and has little preferential splitting (Patton and Carr, 1982). By 1896, Salem Limestone had been used in the construction of buildings and as trim to complement other stones in 25 States (Hopkins and Siebenthal, 1896). Some of the notable buildings constructed of Indiana limestone are listed in table 3. Because of its widespread and continued use and because of its availability, the Salem Limestone was selected as the limestone for the acid deposition exposure studies.

Dimension limestone that is selected for use in a building is specified by its color and grade. The color of the Salem Limestone varies, but it is classified as buff, gray, or variegated (a mixture of buff and gray). Grades are determined by the sizes of the pores and grains that form the texture of the stone. The texture is assessed by visual examination when the stone is graded. Three grades, rustic, standard, and select, are commonly used. Two other grades, gothic and statuary, also have been quarried but rarely are used. Of the three commonly used grades, rustic is the coarsest grained, and select is the finest grained and the most homogeneous in appearance. Although it is difficult to quantify the limits of the three grades, grain size decreases from the rustic through the standard to the select grade, and the pore sizes within each grade are typically more than 2 mm in the rustic, less than 2 mm in the standard, and less than 1 mm in the select (Rooney, 1970). The Salem Limestone block obtained from the Independent quarry near Bloomington, Ind. (Ross and Knab, 1984), is classified as a select buff stone.

GEOLOGIC DESCRIPTION

Shelburne Marble

The Shelburne is of Early Ordovician age and is a low grade, regionally metamorphosed marble that forms part of the marble belt in western Vermont. The Shelburne is interbedded with and overlain by schist. The complexly folded marble beds lie along the Middlebury synclinorium. The marble beds are bounded on the east by the Green Mountains, where low-angle thrust faults dip to the east, and are bounded on the west by the Adirondack Mountains, where thrust faults dip to the west along the northern portion of the marble belt and normal faults dip to the east along the southern portion. The Shelburne varies from sedimentary limestone near the Canadian border to the coarse-grained marble that is quarried in Danby, Vt. The Danby quarry lies in the southernmost of three main structural units that form the marble belt (Bain, 1934). The southernmost structural unit extends from Manchester to Middlebury and is characterized by medium- to coarse-grained marbles in complex flowage and fold structures. The two structural units to the north have experienced less tectonic and metamorphic activity than the southernmost unit. The central structural region of the marble belt lies between Middlebury and Milton and is characterized by fine-textured stone in simple, open folds lying between thrust faults. The northern structural unit, in the vicinity of Plattsburg, N.Y., and Isle la Motte, Canada, is a faulted area of unmetamorphosed sediments.

The Danby quarry in Vermont is the source of the test stone used for this study, and it is also the only producing quarry in the Shelburne Marble. The gently plunging (8°) synclinal structure at the Danby quarry has enabled improvements to be made in quarrying techniques and thus allowed the quarry to be a contender in the world market (Meade, 1980), while other Vermont marble quarries have closed.

The nature of the folding in the marble beds is a significant factor in assessing the commercial value of a particular layer of marble. As the marble beds were folded, the calcite became plastic, and elongation and thinning of the beds along the limbs of the folds and thickening of the beds at the ends of the folds resulted (Dale, 1912, 1914). Locally, a marble layer may thin to inches, and at other places it may thicken to more than 300 ft (Bain, 1959). It is from the thickened beds that large, useable blocks of marble can be removed, and they are thus more likely to be of commercial value than marble taken from thin layers.

Salem Limestone

The Salem is Late Mississippian in age and has an outcrop area in south-central Indiana that is nearly 160 mi long (Donahue, 1967). Stratigraphically, it is above the Harrodsburg Limestone and below the Saint Louis Limestone. The Salem lies horizontal or slopes westward at very low angles (Loughlin, 1929), and it occurs in outcrop as massive rounded ledges that are gray in color and coarsely textured (Rooney, 1970). In some places, the Salem is nearly 100 ft thick, but where dimension stone is quarried it is commonly 40 to 60 ft thick (Smith, 1966). Early quarries in the Salem Limestone were located along or adjacent to stream valleys (Udden, 1909). The quarries today are located where there are thick, homogeneous lenses of material suitable for dimension stone (Patton and Carr, 1982). The lenses or pods of suitable dimension stone are irregularly scattered; in some places, less than a mile from a thick lens, the dimension stone facies may thin or be interrupted (Patton and Carr, 1982). The principle production of dimension stone from the Salem Limestone is in the central third of its outcrop area, between the White River and the East Fork White River in Monroe and Lawrence Counties (Patton and Carr, 1982).

The Salem Limestone comprises three lithologies: (1) a well-sorted, medium- to coarse-grained, massive calcarenite; (2) a poorly sorted calcarenite that ranges in grain size, sorting, and porosity; and (3) an impure carbonate that contains varying amounts of quartz and carbonaceous material (Smith, 1970). The ideal dimension stone from the Salem is massive, even textured, medium grained, and bryozoan rich but has few echinoderm plates and few specimens of the foraminifer *Endothyra* (Smith, 1966). Thus, of the three lithologies described, the first is the one that is used for dimension stone.

The building stone facies of the Salem is light gray to bluish gray but is oxidized to a buff color in massive sections and along bedding planes and joints. Crossbeds are common microscopically and in outcrop; they are characteristic of the Salem Limestone and are well displayed in the weathered stone. Most crossbeds are less than 1 ft high, but they may be between 1 and 3 ft (Patton and Carr, 1982). The stone has a granular texture and a range of grain sizes from fine (<1 mm) through medium (1–3 mm) to coarse (>3 mm), and it is well sorted (Loughlin, 1929). The porous and permeable nature of the limestone makes it an important reservoir for oil in the Illinois basin (Patton and Carr, 1982).

The Salem Limestone has long been discussed in the geologic literature because of its distinctive dwarf fauna, which was first described by Hall (1858). Much has been written about the fossil constituents in an effort to distinguish whether the small sizes were due to stunting or selective sorting (Donahue, 1967). The foraminifer *Endothyra baileyi* is used as a guide fossil to identify the Salem in outcrop and in subsurface samples (Smith, 1970; Patton and Carr, 1982). Although the Salem has been called an oolitic limestone, true oolites are rare (coatings on fossil fragments are usually much less than 20 percent of the diameter (Patton and Carr, 1982)), as are structureless pellets. Both mechanically rounded fossil debris and abundant spheroidal specimens of *Endothyra baileyi* give the stone an oolitic aspect that may have given rise to the misnomer (Rooney, 1970; Smith, 1970).

For many years the name used for the Salem Limestone in Indiana has been a matter of controversy (Smith, 1970); however, for the last 30 years the name Salem Limestone has been consistently used by geologists. Some of the names that have been used and later discarded include Bedford stone, Bedford oolitic limestone, and Spergen limestone (Loughlin, 1929; Smith, 1970). The Salem Limestone also has names that are used in the dimension stone trade, such as Indiana limestone, Indiana oolitic limestone, Bedford stone, and Bedford oolitic limestone (Udden, 1909). Some of these trade names are still in use today, although the most common name is Indiana limestone.

MINERALOGICAL DESCRIPTION

A necessary assumption that underlies the stone exposure program experiment is that the characteristics of the stones are known prior to exposure, particularly those characteristics that may influence the weathering behavior of the stone. Because stone is composed of various constituents (minerals and (or) fossils), it may respond inhomogeneously to liquid and gaseous weathering agents, such as H_2O, H^+, $SO_4^=$, SO_2, and so on. The mineral compositions, shapes, sizes, and associations all may contribute to the stone's resistance to deterioration. Thus, to provide a baseline for our study, we have examined freshly quarried samples from the blocks of Shelburne Marble and Salem Limestone that have been placed at the NAPAP stone exposure sites.

The focus of the mineralogical characterization has been to identify the kinds and compositions of the mineral constituents, as well as their relative abundances, distributions, and associations. Characteristics related to the mineralogy, the bulk composition, the porosity, and some physical measurements, also were determined. The methods used and results of the mineralogical characterization are discussed below. The bulk compositions were obtained by submitting samples of the marble and limestone for whole rock analysis. One average sample of marble was analyzed from the middle of the block (slab H1–3), and four samples of limestone were analyzed, one from the top (AU3), one from the bottom (NU3), and two from the middle (GU3, HU3) of the block. The major and trace elements determined from whole rock analysis of the marble and limestone are shown in tables 4–6. As can be

Table 4. Whole rock analysis of the H1–3 slab, Shelburne Marble

[Analyses made by J.R. Lindsay (U.S. Geological Survey). Major elements determined by X-ray fluorescence; trace elements determined by direct reader direct current arc spectrometry. LOI, loss on ignition]

Major elements (weight percent)	
SiO_2	0.40
Al_2O_3	.20
Fe_2O_3	<.05
MgO	.52
CaO	55.50
Na_2O	<.10
K_2O	.09
TiO_2	.02
P_2O_5	<.03
MnO	<.01
LOI	43.20
Total	99.93

Trace elements (ppm)			
Mn	234	La	56
As	<100	Li	<10
Au	<9.5	Nb	162
B	<9.5	Ni	14
Ba	22	Pb	38
Be	.99	Sb	<100
Bi	<10	Sc	<10
Cd	<?	Se	<200
Ce	218	Sn	<8.4
Co	13	Sr	302
Cr	19	Te	<49
Cu	6.4	V	38
Ga	<9.7	Y	13
Hg	<500	Zn	648
		Zr	51

Table 5. Whole rock analysis of the Salem Limestone

[Rapid rock analysis of major elements by Homer Smith (U.S. Geological Survey). Emission spectrographic analysis of trace elements by A.F. Dorrzapf, Jr., and C.J. Skeen (U.S. Geological Survey)]

Sample	AU3	GU3	HU3	NU3
Major elements (weight percent)				
SiO_2	0.44	0.52	0.48	0.52
Al_2O_3	.19	.48	.18	.17
Fe_2O_3	.10	.18	.13	.12
FeO	.02	<.01	<.01	<.01
MgO	.44	.48	.47	.47
CaO	56.2	55.3	55.4	55.5
Na_2O	.06	.05	.05	.06
K_2O	.22	.13	.12	.15
H_2O^+	.17	.42	.40	.31
H_2O^-	<.01	.05	<.01	.07
TiO_2	.01	.01	.01	.01
P_2O_5	.01	.01	.03	.03
MnO	<.01	<.01	.02	.02
CO_2	43.2	43.1	42.7	43.5
Total	101.15	100.73	99.99	100.93
Trace elements (ppm)				
Ag	0.11	<0.10	0.11	<0.10
Ba	6.0	3.0	3.2	3.2
Co	1.7	1.6	1.3	1.5
Cr	3.7	3.0	6.0	1.6
Cu	1.1	<1.0	<1.0	<1.0
Dy	<22	22	<22	<22
Mn	150	150	140	150
Mo	2.9	3.6	2.9	3.0
Ni	3.8	3.5	3.2	2.5
Sc	3.5	3.6	3.1	3.8
Sr	500	550	540	510
V	6.2	5.8	4.5	6.9
Y	3.8	3.1	3.7	4.1
Zr	6.8	3.9	5.8	5.2

seen from tables 4, 5, and 7, the whole rock compositions of the Shelburne Marble and the Salem Limestone are similar to the compositions of typical Vermont marble and Indiana limestone. Porosity measurements on the marble and limestone samples are shown in table 8. The total porosities of the marble (~0.75 percent) and of the limestone (~18.6 percent) are typical for these rock types (table 8). Physical tests were made on samples of the Salem Limestone block by the Indiana Geological Survey (table 9), but no similar tests were made on samples of the Shelburne Marble block. Similar physical tests were made on commercial marbles (Kessler, 1919) and limestones (Kessler and Sligh, 1927) to establish their value for use in masonry structures. Table 10 summarizes results from some of the tests made by Kessler (1919) and Kessler and Sligh (1927) for a Vermont marble and an Indiana limestone that were taken from quarries near Danby, Vt., and Bedford, Ind., and that are similar to the Shelburne Marble and Salem Limestone samples of this study. The compression and shear strength measurements on the Salem samples from the test block are much lower than the same measurements made by Kessler and Sligh (1927). A similar comparison made by the Indiana Geological Survey (written commun., March 28, 1986) between test Salem Limestone samples and typical Salem Limestone samples showed that the measurements differed significantly only in shear strength; samples from our test block had a lesser shear strength than that of typical Salem Limestone.

Methods Used

For the initial mineralogical characterization, polished thin sections were used to identify minerals and to determine the minerals' composition, distribution, association, and relative abundances. Polished sections of the H1–3 slab (fig. 2*B*) of the Shelburne Marble were chosen to represent the diversity of the random inclusions in the stone. Polished sections of the Salem Limestone represent the top (AU3), bottom (NU3), and middle (GU3, HU3, LU6)

Table 6. Sulfur in Salem Limestone

[Analyses by P.P. Hearn, R.G. Johnson, and Homer Smith (U.S. Geological Survey)]

	AU3	GU3	HU3	NU3
Insoluble residue (weight percent) left after dissolving rock in 5 percent HCl.	0.71	0.89	0.83	0.79
Total sulfur from sulfides (ppm) contained in insoluble residue.	70	170	100	100
Total sulfur from barite (ppm) contained in insoluble residue.	6	1	6	2
Total sulfur as soluble sulfate (ppm) from the 5 percent HCl solution.	<1	<1	<1	<1

portions of the test block (fig. 1*B*). The sections were cut parallel to the bedding. Optical microscopy, modal analysis, scanning electron microscopy, and electron microprobe analysis were used in the mineralogical characterization.

Modal analysis was used to determine the abundances of the individual minerals or fossils. For the marble, this information indicates the abundance of inclusions relative to calcite, and for the limestone, it indicates the abundance of fossils relative to matrix calcite. The results for the marble were combined into groups of mineral types (carbonates, layer silicates, framework silicates, and nonsilicates), and the results for the limestone were grouped by fossil types (echinoderms, bryozoans, other fossils—for example, *Endothyra*, ostracods, gastropods, and brachiopods) and calcite matrix. Miscellaneous categories were used in both point counts to account for points that were difficult to clearly distinguish.

Table 7. Whole rock analyses of typical Vermont marble and Indiana limestone, in weight percent

[Representative Vermont marble and Indiana limestone samples were measured by Kessler (1919; reference no. 10, Danby marble from Danby, Vt.) and Kessler and Sligh (1927; reference no. 46, Standard Buff limestone from near Bedford, Ind.). These examples were selected for comparison because of their similarity and proximity to test stones of this study. LOI, loss on ignition; insol, insoluble in HCl; orgnc, organic matter]

Vermont marble		Indiana limestone	
CaO	55.30	CaO	54.60
MgO	.41	MgO	.68
Fe_2O_3	.03	Fe_2O_3	.05
Al_2O_3	.10	Al_2O_3	.75
SO_3	trace	SO_3	.05
LOI	43.72	Na_2O	.12
insol	.76	SiO_2	.24
		Total S	.85
		LOI	43.57
		orgnc	trace

Table 8. Porosity, in cumulative percent, of the Shelburne Marble and the Salem Limestone

[Measurements by G.R. Olhoeft (U.S. Geological Survey)]

	Shelburne Marble		Salem Limestone	
	K13–01	G22–07	HL2–20	GL3–07
Water accessible	0.332	0.221	17.466	17.398
Helium porosity	.374	.258	17.828	17.689
Total porosity	.807	.731	18.651	18.748

Quantitative chemical analyses of individual mineral phases and fossils were obtained by using an ARL-SEMQ electron microprobe. Standards similar to the unknowns were measured to check on analysis quality, and unknown analyses were judged to be acceptable for silicates, oxides, and sulfides if (1) the oxide total was 98 to 102 and (2) the cation stoichiometry was correct for the mineral analyzed. Several points were analyzed on each grain. Representative occurrences of a mineral were sought to determine if its composition varied with proximity to other mineral phases.

Silicates and oxides were analyzed at 15 KV by using a beam current of 0.1 μa, 20 second counts, and a minimum (1–2 μm) spot size. Bence and Albee (1968) correction procedures with modifications by Albee and Ray (1970) were used, and data were reduced on line (McGee, 1983). The elements that were analyzed varied for each mineral group. Water in layer silicates was calculated (Flohr, 1983) after the on-line data reduction. Sulfides were analyzed by using procedures similar to those used for silicates and oxides; however, a higher accelerating voltage of 25 KV was needed to measure zinc, copper, nickel, and cobalt.

Analysis of carbonates required special analytical conditions because carbonates tend to be unstable under the operating conditions used for silicates and oxides. Thus, carbonates were analyzed by using 12 KV accelerating voltage, 0.05 μa beam current, 20 second counts, and a spot size of ~0.2 mm. Data were reduced on line by using the MAGIC method of Colby (1968). CO_2 amounts were calculated off line for each of the carbonate analyses by using two assumptions: (1) the analysis total (with CO_2 included) equals 100 and (2) CO_2 is the only oxide in the mineral that was not measured by the electron microprobe. Because the oxide totals and mineral stoichiometry of the CO_2-free analyses could not be used directly to check the analysis quality (as they are with silicate and oxide analyses), modified checks were needed. By comparing the

Table 9. Physical measurements of the Salem Limestone

[Measurements are averages of three determinations; ( ), standard deviation; —, measurement not made; measurements were made by the Indiana Geological Survey]

Sample	Hardness to abrasion	Compression (lb/in^2)	Modulus of rupture (lb/in^2)	Specific gravity	Coefficient of absorption (percent)	Shear strength (lb/in^2)
AL1.....	6.46 (0.03)	5,090 (1,600)	—	2.21 (0.006)	5.93 (0.05)	—
GU2.....	6.65 (.32)	4,540 (966)	—	2.22 (.006)	5.92 (.20)	—
NL7.....	6.85 (.10)	5,180 (330)	1,030 (36)	2.23 (.006)	5.89 (.04)	1,290 (15)

Table 10. Physical measurements of typical Vermont marble and Indiana limestone

[Representative Vermont marble and Indiana limestone samples were measured by Kessler (1919; reference no. 10, Danby marble from Danby, Vt.) and Kessler and Sligh (1927; reference no. 14, Select Buff limestone from Bedford, Ind.). These examples were selected because of their similarity and proximity to test stones of this study. Mbl, marble; Ls, limestone; Pp, perpendicular to bedding; pl, parallel to bedding; —, measurement not made. Frozen, tests made on samples that were frozen and thawed 30 times. Porosity is a calculated value; most values are averages of at least two tests]

Sample		Compression			Modulus of rupture (lb/in^2)	Specific gravity	Absorption		Shear strength (lb/in^2)	Porosity
		Dry	Wet (lb/in^2)	Frozen			by weight (percent)	by volume (percent)		
Mbl	Pp.....	10,558	9,944	8,599	1,524	2.71	0.102	0.276	—	0.48
Mbl	pl.....	10,691	10,306	8,734	1,481				—	
Ls	Pp.....	8,350	8,950	—	1,810	2.37	4.2	9.9	2,010	12.9
Ls	pl.....	9,000	9,299	—	1,505				2,000	

standard calcite and dolomite analyses (determined by wet chemical analysis) with the CO_2-free microprobe analyses, good CO_2-free totals for calcite (55–56 weight percent) and dolomite (52–53 weight percent) were determined. A check on the mineral stoichiometry of an analysis was made after CO_2 was calculated, and cation values were redetermined. A good carbonate analysis should have a sum for cations (Ca+Mg+Fe+Mn+Sr) of 1.0±0.2.

Mineralogy of the Shelburne Marble

The Shelburne Marble is composed predominantly of white calcite. Ten other minerals form heterogeneously distributed inclusions in the marble and, as they are commonly intergrown and some are dark in color, give the marble a characteristic streaked appearance (fig. 6). Whole rock analysis of a representative portion of the marble shows that CaO is the dominant component; all other oxides and element concentrations are below 1 weight percent (table 4). The minerals that compose the Shelburne are divided into four groups: carbonates (calcite, dolomite), layer silicates (phlogopite, muscovite, chlorite, talc), framework silicates (quartz, feldspar), and nonsilicates (rutile, pyrite, apatite). A common association is phlogopite + dolomite ± rutile ± chlorite (fig. 7). Averaged modal abundances and modal abundances of the minerals within each sample are shown in table 11: carbonates=97.3 percent, layer silicates=1.8 percent, framework

Figure 6. Slab of Shelburne Marble (dimensions 2×12×24 inches), showing characteristic dark and light streak pattern caused by inclusions in the marble.

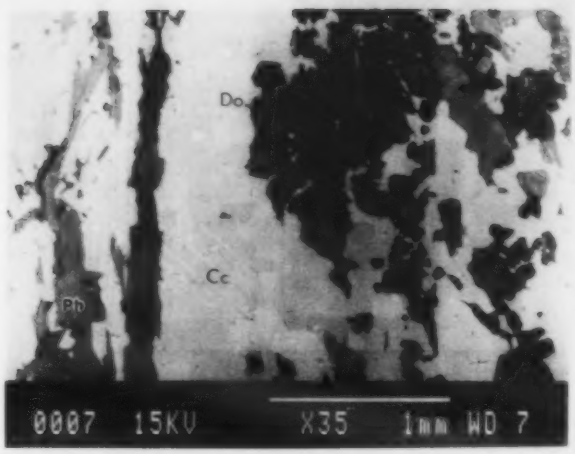


Figure 7. Typical association of phlogopite and dolomite inclusions in the Shelburne Marble. Cc, calcite; Ph, phlogopite; Do, dolomite.

silicates=0.1 percent, nonsilicates close to 0 percent, and pits and holes=0.7 percent. Although talc, quartz, potassium feldspar, rutile, and pyrite were not encountered during point counting, all of these phases were found during petrographic study. Although random areas of the thin sections were counted to determine modal abundances, the sections were made especially to include portions of the dark inclusion streaks. Thus, the abundances determined by modal analysis should be regarded as approximate abundances.

Most of the inclusions are relatively small grains (table 12). Mineral compositions do not vary much (table 13) and are similar to the end member or ideal composition for that mineral. A description of each mineral in the Shelburne Marble is given below, and representative analyses of each phase are shown in table 14.

Carbonates.—Although the Shelburne Marble is predominantly (~97 percent) calcite, it also contains dolomite (~0.6 percent). The calcite is white in hand specimen and is unzoned and inclusion free in thin section. The calcite grains are equidimensional but vary in the largest dimension from 290 to 860 μm; grain widths vary over relatively short distances, and within the scale of a thin section they commonly vary by 300 μm. Grains are irregularly shaped, have subangular to slightly curved edges, and are tightly interlocked. Calcite twinning is common, but much of it probably was caused by sample preparation. Compositionally, the calcite is fairly pure $CaCO_3$ and has an MgO content that averages 0.8 weight percent (tables 13 and 14).

Dolomite is light to dark gray in hand specimen, but in thin section it has a speckled appearance that results from numerous tiny black inclusions. Dale (1912) identified one type of marble as graphitic calcite marble. The inclusions are probably graphite, but in this study they have not been positively identified because they are of submicron size and are not at the surfaces of the grains. Dolomite grains are irregularly rounded in shape and range in diameter from 10 to 290 μm (table 12). They are commonly found in clusters with or without phlogopite, but solitary grains of dolomite surrounded by calcite grains are also present. The association of dolomite + phlogopite grains gives the marble its

Table 11. Modal abundances in samples of the Shelburne Marble, in percent

	Samples				
	H13–N–6	H13–N–7	H13–N–8	H13–N–9	H13–N–10
Carbonates					
Calcite	98.3	95.4	96.5	98.8	94.2
Dolomite	0	0	1.6	0	1.5
Layer silicates					
Phlogopite	.2	3.3	.6	.2	2.9
Muscovite	0	.1	.1	.4	0
Chlorite	.1	.7	.2	.1	.6
Talc	0	0	0	0	0
Framework silicates					
Quartz	0	0	0	0	0
Sodium feldspar	.1	0	.3	0	0
Potassium feldspar	0	0	0	0	0
Nonsilicates					
Rutile	0	0	0	0	0
Pyrite	0	0	0	0	0
Apatite	0	.1	0	0	0
Pits, miscellaneous	.4	.3	.2	.3	.7
Holes	.7	.2	.3	.3	.1

characteristic streaked appearance (figs. 6 and 7). The dolomite composition is very close to the ideal $CaMg(CO_3)_2$, although dolomite in the samples contains very small amounts of FeO (~0.3 weight percent) (tables 13 and 14).

Layer silicates.—Layer silicates (phlogopite, muscovite, chlorite, talc) are the second most abundant mineral group in the Shelburne Marble (0.3–4 percent; table 11). None of the layer silicates has a large compositional range (fig. 8). Because the layer silicates form linear clusters of thin blades, they give the marble its distinctive wavy streak pattern.

Phlogopite is by far the predominant layer silicate phase. In hand specimen it has a pale brown color and, with dolomite, is readily visible in the colored streaks of the marble. Optically, the phlogopite is only weakly pleochroic (very pale brown to white), and thin blades of phlogopite grains are intergrown together. Phlogopite + dolomite ± chlorite is a common association, but phlogopite also occurs as small isolated grains. Phlogopite blades range from 20 to nearly 600 μm in length (table 12) but are commonly 150 to 300 μm long. Phlogopite is magnesium rich (MgO=25.8–28.0 weight percent) (tables 13 and 14) and contains minor amounts of FeO (~0.6 weight percent), TiO_2 (~0.3 weight percent), and fluorine (~2.4 weight percent).

Muscovite is relatively rare. It is small (10–100 μm in length; table 12) and occurs as sparsely scattered colorless grains. Muscovite contains a small amount of MgO (2–3 weight percent) and very minor amounts of CaO (~0.4 weight percent) and TiO_2 (0.5–0.9 weight percent) (tables 13 and 14) and is close to the ideal muscovite composition.

Chlorite is nearly as rare as muscovite, but the grains are larger (~50–200 μm long; table 12), and it is usually intergrown with phlogopite (or with phlogopite and dolomite). The grains are colorless in thin section. Compositionally, the chlorite belongs to the clinochlore group because it contains 32.3–33.3 weight percent MgO, only ~1 weight percent FeO (tables 13 and 14), and ~5.8 silicon cations.

Talc is rare but notable because the grains are large (400–530 μm long; table 12). It is colorless in hand specimen and in thin section. The talc is in inclusion-rich areas, and it is most closely associated with quartz and dolomite. It is nearly ideal in composition (tables 13 and 14) and contains very minor amounts of Al_2O_3 (0.2–0.4 weight percent), FeO (~0.3–0.4 weight percent), and fluorine (0.5–0.7 weight percent).

Framework silicates.—Framework silicates in the Shelburne Marble include feldspar and quartz, which constitute up to 0.3 percent of the marble. Both feldspar and quartz are rounded, colorless, 30- to 150-μm grains (table 12). They are usually found as isolated grains, although they may be present also in inclusion-rich areas. Quartz is nearly pure SiO_2 (tables 13 and 14). Sodium feldspar is the primary feldspar in the Shelburne Marble, and it is commonly 50 to 100 μm in diameter. A minor amount of small (30–40 μm) potassium feldspar is present too. Both feldspars are very close to their respective ideal compositions (tables 13 and 14).

Nonsilicates.—Rutile, pyrite, and apatite compose the nonsilicates in the Shelburne Marble. All are rounded, small grains; rutile and pyrite are similar in size (10–60 and 10–40 μm in diameter, respectively), but apatite is a little larger (30–100 μm) (table 12). Rutile and apatite are colorless and best seen in thin section. Large grains of pyrite are visible in hand specimen, but they are rare. Pyrite is not framboidal in the unexposed marble; the surface texture of the pyrite is nearly indistinguishable from that of

Table 12. Largest dimensions of mineral grains (μm) for the Shelburne Marble

	Samples				
	H13–N–6	H13–N–7	H13–N–8	H13–N–9	H13–N–10
Carbonates					
Calcite	700–860	350–570	450–570	290–570	360–500
Dolomite		20	10–90	60–290	20–180
Layer silicates					
Phlogopite		40–500	25–580	80–375	20–480
Muscovite	10–40	20–100	20–30		
Chlorite		50–70	100–200		60–100
Talc				530	400
Framework silicates					
Quartz	40–100			150	50–70
Sodium feldspar	40–75	50–150	15–75		130
Potassium feldspar	30–40				
Nonsilicates					
Rutile		10–50	10–35	60	40
Pyrite		10–40			
Apatite		30			40–100

Table 13. Compositional ranges of minerals in the Shelburne Marble, in weight percent

[( ), number of grains analyzed]

Oxide	Carbonates			
	Calcite (42)		Dolomite (11)	
	Minimum	Maximum	Minimum	Maximum
CaO	53.59	55.94	29.84	34.09
MgO	.21	1.28	18.37	21.72
MnO	0	.01	0	0
FeO	0	.37	.18	.65
SrO	0	.32	0	.25
CO_2[1]	43.29	44.97	47.15	48.21

Oxide	Layer silicates							
	Phlogopite (34)		Muscovite (4)		Chlorite (5)		Talc (3)	
	Minimum	Maximum	Minimum	Maximum	Minimum	Maximum	Minimum	Maximum
SiO_2	41.67	44.57	48.96	49.84	30.41	31.37	62.05	63.44
Al_2O_3	12.15	15.12	30.20	33.56	20.23	21.50	.16	.36
K_2O	9.69	10.90	10.28	10.47	0	.71	0	0
CaO	.03	.53	.33	.49	.03	.19	.09	.16
MgO	25.76	27.97	2.32	3.34	32.34	33.26	30.70	31.54
FeO	.52	.76	.10	.12	.86	1.13	.29	.35
BaO	0	.11	.11	.18	0	.04	0	.04
TiO_2	.22	.42	.52	.88	0	.07	.05	.07
Na_2O	.04	.22	.11	.14	0	.02	.05	.06
MnO	0	.02	0	.02	0	.02	0	.04
F	2.06	2.83	.13	.17	.36	.49	.45	.66
H_2O[1]	2.98	3.41	4.41	4.57	12.66	12.74	4.44	4.45

Oxide	Framework silicates			
	Feldspar (28)		Quartz (10)	
	Minimum	Maximum	Minimum	Maximum
SiO_2	67.25	69.63	98.07	101.50
Al_2O_3	19.28	20.35	0	.05
Na_2O	11.31	12.13	0	.04
CaO	.03	.60	0	.05
K_2O	.03	.11	0	.03
BaO	0	.04	.06	.38
FeO	0	.03	0	.13
MgO	0	.01	0	.10

Oxide	Nonsilicates			
	Rutile (8)		Element	Pyrite (5)
	Minimum	Maximum		Minimum	Maximum
TiO_2	96.55	98.35	Fe	45.30	45.76
Cr_2O_3	0	.14	S	52.43	52.99
Al_2O_3	0	.04	Cu	0	0
FeO	0	.18	Zn	0	0
MgO	0	.08	Co	.06	.20
MnO	0	0	Ni	0	0
NiO	0	.02			
CaO	.21	2.01			
SiO_2	0	.08			

[1]Calculated value.

Table 14. Representative mineral compositions in the Shelburne Marble, in weight percent

	Carbonates	
Oxide	Calcite	Dolomite
CaO	54.87	30.66
MgO	.78	21.05
MnO	0	0
FeO	.05	.31
SrO	.10	.03
CO_2[1]	44.20	47.95
Total	100.00	100.00

	Layer silicates			
Oxide	Phlogopite	Muscovite	Chlorite	Talc
SiO_2	42.60	49.07	30.54	62.52
Al_2O_3	14.64	30.20	20.82	.20
K_2O	10.45	10.47	0	0
CaO	.25	.33	.19	.09
MgO	26.00	3.34	33.26	30.96
FeO	.69	.12	1.09	.34
BaO	0	.11	0	.02
TiO_2	.35	.55	0	.05
Na_2O	.05	.13	0	.05
MnO	0	.01	0	.02
F	2.14	.17	.39	.53
H_2O[2]	3.29	4.41	12.73	4.44
Total	100.46	98.91	99.02	99.22

	Framework silicates		
Oxide	Sodium feldspar	Potassium feldspar	Quartz
SiO_2	68.08	65.02	99.05
Al_2O_3	19.90	18.91	0
Na_2O	11.76	.26	.01
CaO	.19	.16	.13
K_2O	.09	16.55	0
BaO	0	.16	.04
FeO	0	0	0
MgO	0	0	0
Total	100.02	101.06	99.23
Ab	98.62	2.30	
An	.89	.80	
Or	.49	96.89	

	Nonsilicates		
Oxide	Rutile	Element	Pyrite
TiO_2	98.09	Fe	45.42
Cr_2O_3	.02	S	52.83
Al_2O_3	.04	Cu	0
FeO	.07	Zn	0
MgO	.07	Co	.13
MnO	0	Ni	0
NiO	.02	Total	98.38
CaO	.59		
SiO_2	0		
Total	98.90		

[1] CO_2 calculated by difference and stoichiometry.
[2] H_2O calculated on the basis of site occupancies.

the surrounding calcite in the secondary electron image (fig. 9). Rutile, pyrite, and apatite may occur as isolated grains or may be associated with phlogopite in inclusion-rich areas (fig. 10). In one sample, rare sphene (~20 μm) is associated with rutile ± quartz in an inclusion-rich area. The distribution of the nonsilicates is heterogeneous; pyrite grains are commonly localized in small areas. Rutile is the most widely distributed of the three phases, and apatite is a very minor inclusion. Rutile is nearly pure TiO_2 (tables 13 and 14), although it does contain some CaO (~1.2 weight percent), which may be due to the small grain size and overlap effects with calcite during analysis. Pyrite is homogeneous in composition (tables 13 and 14) and contains iron (~45.5 weight percent), sulfur (~52.7 weight percent), and minor cobalt (~0.12 weight percent).

Mineralogy of the Salem Limestone

The Salem Limestone is a very pure calcium carbonate limestone. Whole rock analyses, fossil compositions, and the kinds and compositions of the minerals in the stone

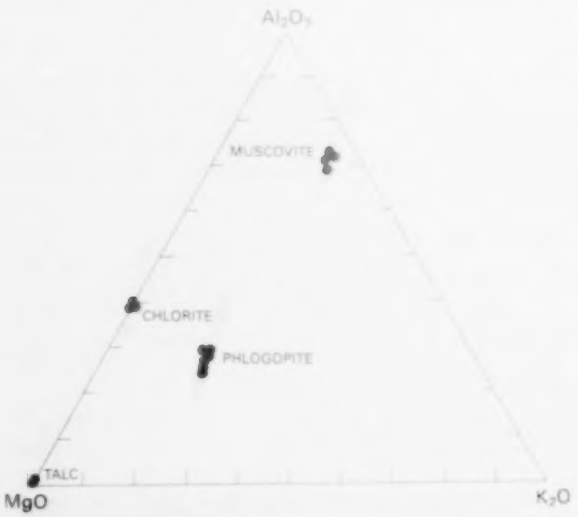


Figure 8. Al_2O_3-K_2O-MgO ternary diagram that shows chemical compositions of layer silicate minerals in the Shelburne Marble.

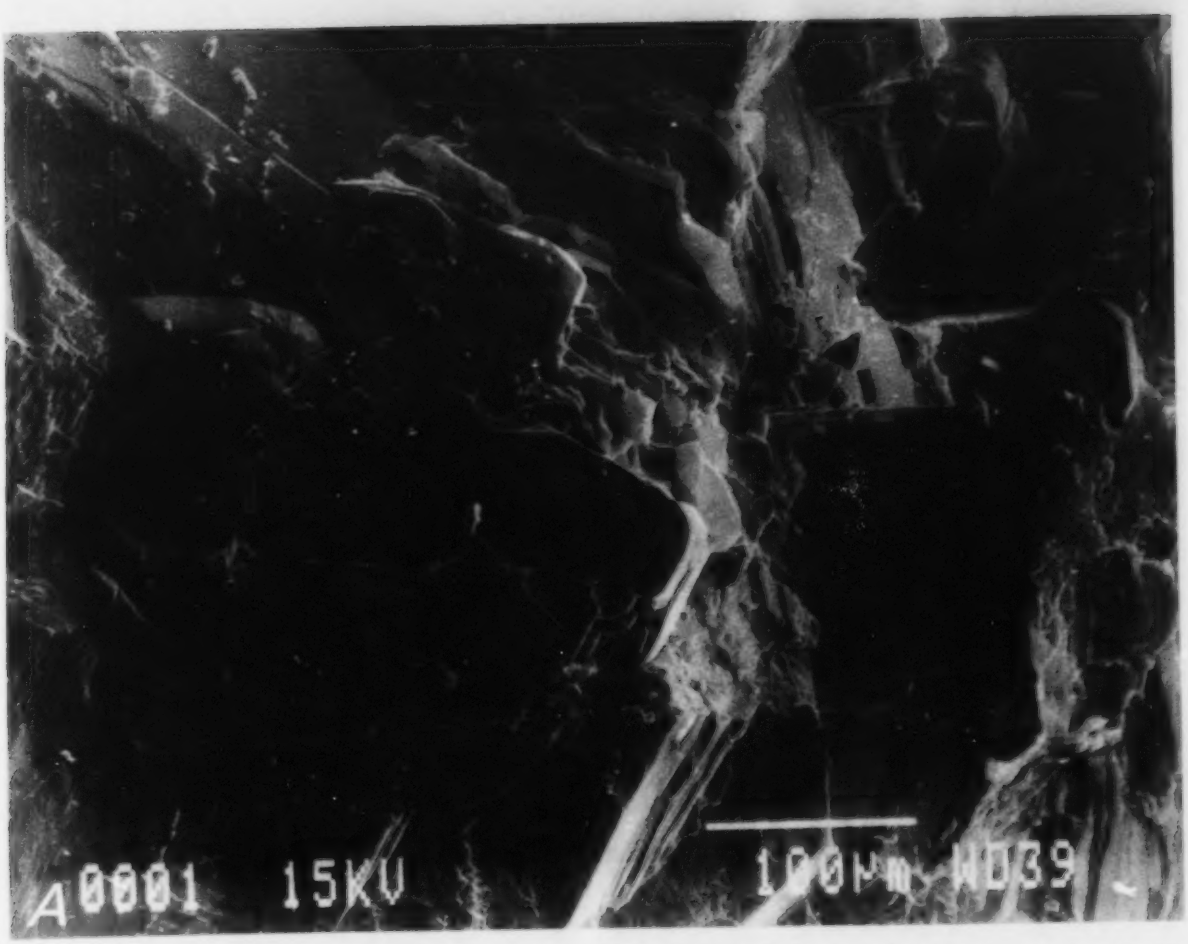


Figure 9. Pyrite and calcite on a fracture surface of unexposed Shelburne Marble. *A*, In the secondary electron image, surficial characteristics of pyrite are indistinguishable from those of the calcite (compare with *B*).

reveal that the limestone contains little besides calcite-cemented fossils. Whole rock analyses of four samples from the test block show that the limestone averages 55.6 percent CaO and that the CaO content varies only slightly throughout the block (table 5). The average MgO content is 0.47 percent, and it too varies only slightly in the test block (table 5). The unexposed limestone also contains SiO_2 (0.44–0.52 percent), Al_2O_3 (~0.18 percent with one exception), K_2O (0.12–0.22 percent), and strontium (500–550 ppm). Most of the sulfur measured in the unexposed stone is contributed by sulfides (70–170 ppm; table 6).

The limestone is well sorted and even grained (fig. 11); the average fossil size is 0.2 to 0.5 mm, but in some areas 0.7-mm fragments are common. Whole fossils and fossil fragments are cemented by calcite, and mineral phases other than calcite are rare. Modal analysis of the samples indicates that the stone is composed of nearly equal amounts of echinoderm pieces and bryozoan fragments (29.9 percent and 27.2 percent, respectively; table 15). The calcite matrix is the next most abundant constituent (15.1 percent), followed by miscellaneous fossils (11.8 percent), voids (10.0 percent), other fossils (3.9 percent), and pellets (2.0 percent). The miscellaneous fossils category includes fragments of fossils that were too small to positively identify but are most likely bryozoan fragments, echinoderms, small pellets, and algae pieces. The category "other fossils" includes *Endothyra*, ostracods, gastropods, and brachiopod pieces. Calcite was the only mineral phase encountered during point counting, but rare grains of quartz, feldspar, and hematite or magnetite were found during examination of the stone. The proportions of fossils found in these samples are similar to the results obtained by Smith (1962) in his study of more than 100 sections of Salem Limestone from various locations in Indiana. He found that most samples have a larger volume of fossil constituents than binding material and that bryozoans are

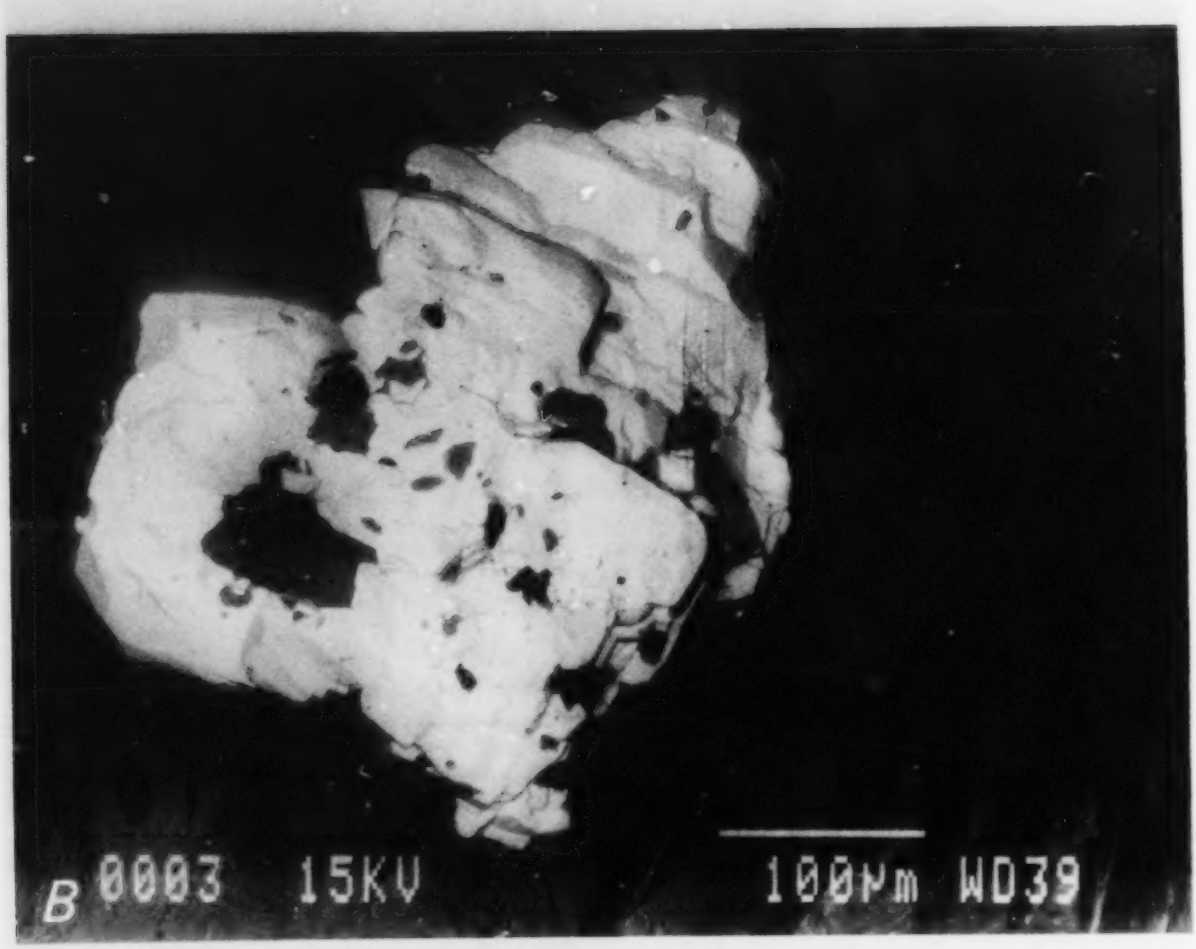


Figure 9.—Continued. *B*, In the backscattered electron image of *A*, the pyrite appears white compared to the calcite.

the most abundant fossil material, followed by echinoderms. Smith (1962) reported that miscellaneous fossils, bryozoans, and echinoderms are well mixed throughout the samples of Salem Limestone and concluded that the unclassifiable fossils are most likely bryozoans and echinoderms because these two fossils have the best representation in the Salem Limestone.

Echinoderms.—Plates, spines, and columnal segments of echinoderms are present in the test block (fig. 12). The plates are the most abundant echinoderm piece, are generally square to elongate in shape, and measure from 0.3×0.2 to 0.9×1.5 mm. Plates that measure 0.3×0.5 and 0.9×1 mm are the most common, however. Oblique sections of echinoderm spine pieces (fig. 13) are elongate and measure approximately 1.5×0.3 mm, although some measure up to 3.8×0.3 mm. Echinoderm columnal segments are readily recognizable but are not as abundant as the plates. The columnals range in size from 0.3 to 1.4 mm in diameter. The echinoderm pieces are composed of calcite and do not differ in composition from the matrix calcite that surrounds them. Indeed, many of the echinoderm pieces are surrounded by large single grains of calcite that are in optical continuity with the fossil fragment. The echinoderm pieces predominately contain CaO, only small amounts of MgO (0.49–0.68 weight percent), and variable SrO (0.0–0.44 weight percent; tables 16–18). Echinoderm spines and columnals contain slightly less MgO than the echinoderm plates (table 18). Although the SrO contents of the various echinoderm pieces vary, there is no correlation between SrO content and type of fossil fragment.

Bryozoans.—Bryozoans are most commonly found in the sample as fragments of stems, but occasionally portions of fenestra have been preserved (figs. 12 and 14). The bryozoan pieces are elongate in shape, and they range greatly in size. A common size is approximately 1.0×0.2 mm, but pieces that are up to 1.4 mm long are not unusual. The fenestra that have survived are variable in degree of preservation and in size; pieces are about 1.0×1.5 mm in

Figure 10. Typical association of pyrite and phlogopite in the Shelburne Marble. Cc, calcite; Ph, phlogopite; Py, pyrite.

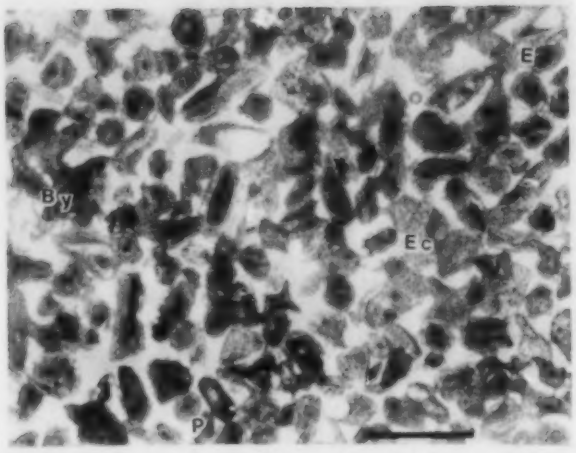


Figure 11. Transmitted light image of fossil fragments in sample LU6D of the Salem Limestone. Note the homogeneous sizes of the fragments. Echinoderm plates (Ec) and bryozoan fragments (By) are abundant; *Endothyra* (E) and pellets (P) are also present. Scale bar=1 mm.

size, but one piece is 3.7×2.3 mm. Compositionally, the bryozoans are about 55 weight percent CaO, slightly more than 0.5 weight percent MgO, and slightly less than 0.5 weight percent SrO (tables 16 and 17). Because of the abundance of bryozoans and because they could easily have fractured into pieces that would be difficult to identify with certainty, it is very likely that many of the pieces counted as miscellaneous fossils during modal analysis are actually small fragments of bryozoan stems.

Other fossils.—The remaining fossils in the Salem Limestone form a minor (less than 5 percent) component of the fossil content, but they are notable because in most cases they are preserved as whole or nearly whole specimens.

The foraminifer *Endothyra* has been widely used as an index fossil to identify the Salem. *Endothyra* is not particularly abundant in the test stone (1 percent of points counted), but because it is easy to identify, especially in field and laboratory studies, it has been useful to researchers (Smith, 1962). In the test stone, *Endothyra* individuals are quite uniform in size (0.3 mm in diameter) and appearance (fig. 11). Compositionally, *Endothyra* is nearly pure calcite, has only 0.5 weight percent MgO, and has less than 0.1 weight percent of all other elements (table 17).

Ostracods are preserved in the Salem as partial and whole specimens and are unusually striking in thin section (fig. 15). The inner part of the shells is usually empty but is sometimes lined with small calcite crystals. The ostracods are commonly elliptical in shape and are approximately 0.6×1.0 mm in size. It is likely that the ostracods contrib-

Table 15. Modal abundances in samples of the Salem Limestone, in percent

[No quartz or minerals other than calcite were found during point counting]

	AU3C	AU3D	GU3C	HU3D	LU6D	NU3C	NU3D	Total average
Bryozoan	27.3	27.4	19.4	32.3	27.8	28.9	27.1	27.2
Echinoderm	26.5	26.5	38.9	30.7	26.0	28.0	33.3	29.9
Other fossils								(3.9)
Endothyra	.6	.2	2.0	.4	.7	.8	2.1	1.0
Ostracod	.5	.8	2.8	.2	.4	.4	2.1	1.0
Gastropod	.8	.6	.7	0	.3	.7	.2	.5
Brachiopod	1.0	2.3	2.5	.8	.7	.7	2.0	1.4
Void	9.9	10.8	10.5	11.4	9.1	11.3	7.2	10.0
Calcite matrix	19.2	18.0	8.9	14.0	19.7	12.3	13.8	15.1
Pellet	.9	1.8	5.0	.7	1.2	.9	3.8	2.0
Miscellaneous fossils	13.3	11.7	9.3	9.5	14.3	16.1	8.5	11.8
Total points	1,169	1,153	1,049	1,039	1,058	1,028	1,076	7,552

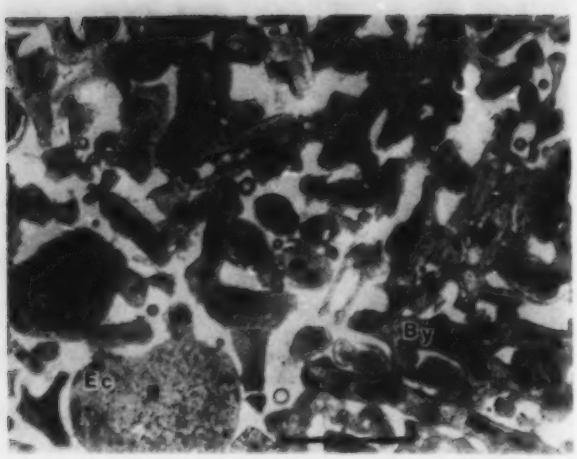


Figure 12. Echinoderm fragments and bryozoan pieces are typically mixed in the Salem Limestone, sample AU3D. Note echinoderm columnal (Ec) in lower left and partial bryozoan fenestra (By) in lower right. Scale bar=1 mm.

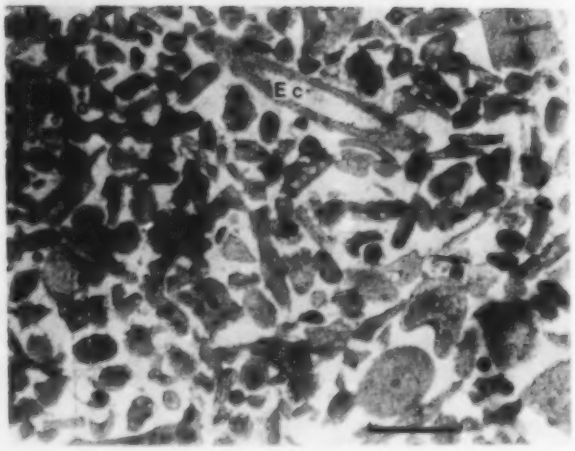


Figure 13. Oblique section of an echinoderm spine piece (Ec), sample AU3D, Salem Limestone. Scale bar=1 mm.

ute to the inhomogeneous appearance of some of the lower grades of Salem Limestone (for example, perhaps forming the "glass spots" mentioned by Loughlin, 1929). The ostracods are similar compositionally to the other fossil constituents of the Salem Limestone (tables 16 and 17).

Gastropods constitute about 0.5 percent of the limestone. They are preserved as whole or nearly whole specimens and are commonly filled with a very fine dark material that resembles mud (fig. 16). Gastropods in the samples contain so much of this very fine dark material and pitting (and occasional identifiable grains of quartz) that it was not possible to obtain any good analyses of the gastropods. The gastropods range in size from 0.3 to 0.7 mm in diameter.

Matrix calcite.—Calcite cement fills spaces between fossil fragments and lines pore spaces in the Salem Limestone. Compared to the fossil fragments in polished sections, the matrix calcite is clear and unpitted. The matrix calcite either surrounds and is in optical continuity with echinoderm fragments or it occurs as rounded grains, ~20 to 50 μm in diameter, between fossil pieces. Compositionally, the matrix calcite is nearly pure (CaO=54.84 to 55.92 percent, MgO <1 percent), and it does not differ much from the fossil compositions (tables 16 and 17).

Other mineral phases.—Quartz and hematite are present in the Salem Limestone as small inclusions in fossil fragments, particularly in echinoderm columnals and bryozoan stem pieces (fig. 17*A*,*B*). Quartz grains are angular and range in size from 10 to 50 μm commonly measuring 10 to 20 μm. Hematite is rounded and irregularly shaped, ranging in size from 10 to 100 μm but commonly 10 to 20 μm. Identification of the hematite is tentative, because, although iron was detected by using energy dispersive analysis on the scanning electron microscope, good quantitative analyses of the grains were not obtained. Small amounts of silicon in some hematite inclusions were detected (fig. 17*C*) and may indicate the presence of minute quartz grains within the pitted areas of the fossil fragments. Pitted areas of the fossil fragments were avoided during electron microprobe analysis because the poor sample surface always produced poor mineral analyses. Although minute mineral inclusions are not reflected in the overall composition of the stone (or the fossils), they may play a significant role in the weathering behavior of the fossil fragments in the limestone.

Table 16. Range of fossil and mineral compositions in the Salem Limestone, in weight percent

[( ), number of fragments or grains analyzed]

Oxide	Bryozoan (6)		Echinoderm (11)	
	Minimum	Maximum	Minimum	Maximum
CaO	54.00	55.52	54.60	55.43
MgO	.29	.93	.36	.95
MnO	0	.12	.01	.08
FeO	.01	.22	.02	.14
SrO	.12	.49	0	.44
CO_2[1]	43.76	44.66	43.52	44.61
Oxide	**Ostracod (3)**		**Matrix calcite (14)**	
	Minimum	Maximum	Minimum	Maximum
CaO	54.88	55.76	54.84	55.92
MgO	.56	.98	.45	.88
MnO	.02	.05	.03	.09
FeO	.04	.08	.01	.11
SrO	.03	.14	0	.25
CO_2[1]	43.59	44.00	43.24	44.76

[1]Calculated value.

Table 17. Representative analyses of fossil fragments and calcite in the Salem Limestone, in weight percent

Oxide	Bryozoan	Echinoderm	Ostracod	*Endothyra*	Matrix calcite
CaO	54.98	55.41	54.88	55.39	55.18
MgO	.62	.55	.98	.53	.68
MnO	.03	.05	.02	.04	.05
FeO	.15	.09	.06	.03	.10
SrO	.39	.16	.06	.09	.07
CO_2[1]	43.84	43.75	44.00	43.91	43.92

[1] CO_2 calculated by difference and stoichiometry

Voids.—The Salem Limestone is a relatively porous material; voids constitute 10 percent of the rock volume (table 15). A more accurate measure of the proportion of voids in the stone is shown by the porosity measurements (table 8). The samples have a total porosity of ~18.7 percent, slightly higher than the porosity measurement by Kessler and Sligh (1927), but within the range of porosities determined for all of the select buff limestones from Indiana (Kessler and Sligh, 1927, table 12). Connected pore space (water accessible porosity) constitutes 17.5 percent of the total porosity of our Salem Limestone samples (table 8), while only 0.8 to 1.4 percent of the total porosity is contributed by isolated pores. The connected pore space may play a significant role in the stone's response to weathering because the connected pores may act as channels for the movement of liquid in the stone; rain may be readily transported into the stone along the interconnected pores. Incomplete filling by matrix between fossil fragments forms the connected pore space in the limestone and presents a large surface area where material may be dissolved or precipitated within the stone.

STONE DURABILITY

Building stone durability depends on factors that include natural defects in the stone, structure design, faulty selection or improper use of the stone, and macro- and microenvironmental conditions where the stone is used. Studies made in the late 1800's and early 1900's show that geologists, architects, and others concerned with the building stone industry were aware of many of these factors (for example, Julien, 1884; Kessler, 1919; Kessler and Sligh, 1927; Loughlin, 1929; Schaffer, 1932). In an early study of the relative durability of building stones in New York City, Julien (1884) noted certain characteristics of the stones (coarseness of grain size, presence of fossils or oolites), as well as architectural flaws (lack of drips, use of flat sills rather than sloped sills) that appeared to lead to accelerated deterioration of some stones. All stones used in buildings are exposed to physical and (or) chemical weathering agents that work on any inherent weaknesses in the stone. Physical weathering processes include rain, wind, ice, and organisms.

Chemical weathering processes such as hydration, hydrolysis, oxidation, reduction, and exchange reactions (Reiche, 1950; Ollier, 1975) are likely to cause mineralogical changes. Chemical weathering processes are of a particular concern because the objective of the stone exposure program is to determine the contribution of acid precipitation to the weathering of building stones. Thus, it is expected that solution, hydrolysis, and cation exchange will be important processes in the deterioration of the stones. The interaction between physical and chemical weathering processes is significant, however, and cannot be ignored in a study of stone deterioration.

The varied susceptibility of minerals to alteration in the weathering environment will influence how the stone responds to the environment. Because the Shelburne Marble and the Salem Limestone are composed so predominantly of

Table 18. Echinoderm chemical analyses, in weight percent, by type of fragment in the Salem Limestone

[( ), number of fragments analyzed]

Oxide	Columnal (3)		Plate (7)		Spine (1)
	Minimum	Maximum	Minimum	Maximum	AU3D-2-1
CaO	54.93	55.43	54.60	55.38	54.80
MgO	.36	.55	.46	.95	.91
MnO	.01	.06	.01	.08	.01
FeO	.07	.10	.02	.14	.12
SrO	.04	.41	0	.44	.17
CO_2[1]	43.52	44.61	43.71	44.48	43.99

[1] Calculated value

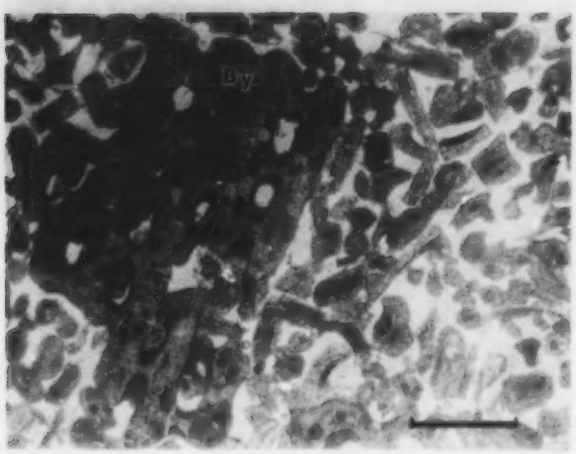


Figure 14. Large pieces of bryozoan fenestra (By) in the Salem Limestone. Sample AU3D, scale bar=1 mm.

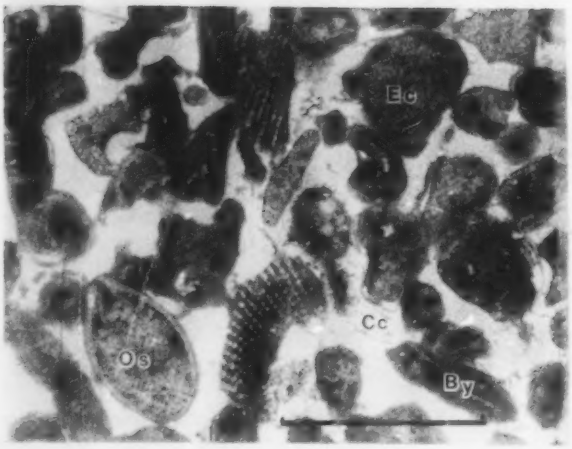


Figure 15. Ostracod (Os), echinoderm plates (Ec), and bryozoan fragments (By). Note matrix calcite (Cc) between echinoderm pieces in right half of photograph. Salem Limestone, sample GU3C, scale bar=1 mm.

calcite, dissolution of calcite under acidic conditions will be a significant component of the weathering processes that act on the stones. However, the degree to which calcite dissolution is important in the overall durability of the stones is influenced by a number of other factors. Dolomite, the layer silicates, and possibly pyrite are also likely to play a significant role in the weathering of the marble as they react with water, pollutants, and one another in the marble. When determining the rates of weathering in minerals, crystal size, crystal shape, crystal perfection, and access of the weathering agent and removal of weathered products are important factors to consider, in addition to composition and structure (Ollier, 1975).

The Shelburne Marble is medium to coarse grained and contains a variety of mineral inclusions that are heterogeneously distributed throughout the rock and are clustered together in linear streaks. On the basis of his examination of buildings in New York City, Julien (1884) estimated the life of coarse dolomitic marble to be 40 years, for fine dolomitic marble to be 60 to 80 years, and for fine marble to be 50 to 200 years. Dale (1912) recognized the significance of grain size and shape to stone durability. He suggested that, although fine-textured marbles present more surface area to rainwater, water can travel rapidly in a coarse-textured loosely compacted marble and thus readily weather the coarse marble. Bain (1941) also identified the width of intergranular openings in marble as a significant factor in the rate of marble weathering because of accessibility to water provided by the cracks. A similar accessibility to water is present around the grain boundaries of large flakes or crystals of silicate inclusions in marble (Dale, 1912). Pore space and cracks are rare in the marble, and calcite grain boundaries are difficult to distinguish using scanning electron microscopy. Where calcite grains meet inclusions, the boundaries are more visible because of slight differences in texture and grain shapes. Although the Shelburne Marble is tightly compacted and not very porous, the movement of water along grain boundaries, especially where large silicate inclusions are present, can be significant. Lewin and Charola (1981) studied a dolomitic marble containing large platy or fibrous inclusions and concluded that it is particularly susceptible to the effects of freezing and thawing when the inclusions are present, resulting in a blistered and pitted appearance on the stone surface. It is likely that the inclusions will weather preferentially in the Shelburne Marble or that their presence will contribute to increased intergranular water in local areas. A preliminary examination of Shelburne Marble columns on the Jefferson

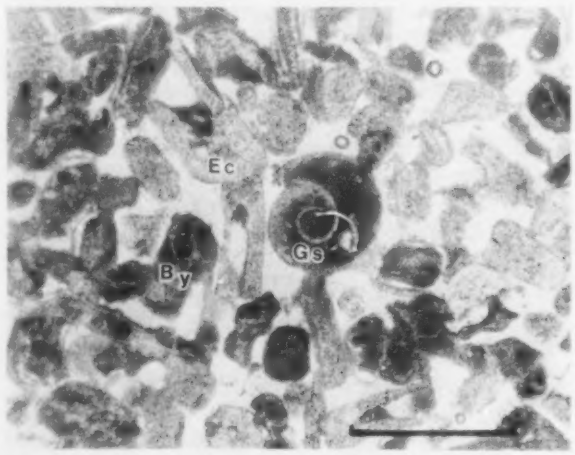


Figure 16. Gastropod (Gs), echinoderm plates (Ec) and spines, and bryozoan fragments (By). Salem Limestone, sample NU3C, scale bar=1 mm.

Figure 17A. Backscattered electron image of a polished section of Salem Limestone. Bryozoan stem (By), echinoderm pieces (Ec), and matrix calcite (Cc). Matrix calcite is light gray and is between the larger fossil pieces. Note small round grains of calcite lining the pore (black) spaces. Note the pitting in the fossil fragments as compared to the matrix calcite.

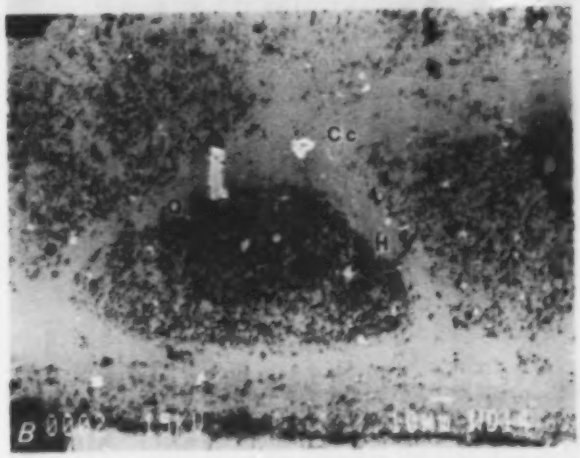


Figure 17B. Close up of the pitting in the bryozoan stem in *A*. Calcite (Cc) is light gray, quartz (Q) is darker gray, hematite (H) is white, fine black areas are pitting, and large continuous black areas are pore spaces.

Memorial in Washington, D.C., has revealed pock marks and grooves that mimic the silicate inclusion pattern (fig. 18); some of which still contain small flakes of mica. Thus due to the hydrologic properties of grain boundaries, the presence of inclusions may be more significant to the deterioration of the stone in buildings than the dissolution of the calcite.

The Salem Limestone has a homogeneous composition and a uniform grain size. Such homogeneity may cause the stone to weather more uniformly than the marble and eliminate the problems of preferential deterioration. However, although the limestone is mineralogically homogeneous and has matrix and fossil constituents composed of calcite, observation of older buildings shows that with time, the matrix erodes away preferentially, leaving the fossils standing in relief. Similar preferential weathering of fossiliferous limestone has been noted in laboratory experiments of weathering, as well (Loughlin, 1929). The fossils may be slightly different compositionally from the matrix and thus more resistant. The analyses of the fossils and matrix in our limestone samples show minor variations of some elements, particularly magnesium and strontium (table 17). However, the amounts are small, and the variations in composition are irregular; no fossil type is consistently higher in minor amounts of an element than another fossil type or than the matrix. The calcite in the fossil fragments has a pitted appearance in polished section compared with the calcite that forms the matrix; the pitting indicates that the fossils were slightly more resistant to the grinding and polishing used in making the sections. Such resistance may be similar to the resistance the fossils show when exposed to weathering conditions. Some fossil fragments, particularly echinoderm columnals and bryozoan stems, contain very small quartz grains and (or) very small hematite(?) grains that also may cause those fossils to be slightly more resistant to weathering. Loughlin (1929) cited an example of silicified coral shells in a limestone building in New York City that protrude as much as 1/16 of an inch above the building surface after 40 years of exposure. Carbonaceous material within the fossils also may make the fossils more resistant to dissolution than the surrounding calcite matrix.

Porosity is another important characteristic of limestone that may lead to accelerated or preferential weathering. Limestone is much more porous than marble, thus giving weathering agents access to more surface area and increasing the likelihood that matrix calcite will dissolve

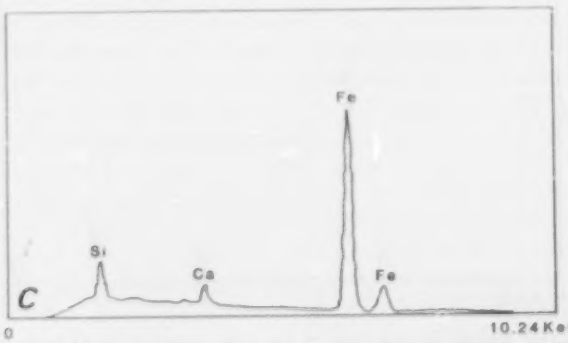


Figure 17C. Energy dispersive spectra of bright white inclusion in *B*, showing that it is composed mostly of iron. A small calcium peak is probably due to overlap with calcite; the silica peak may be an impurity or may signify that there is minor quartz.

Figure 18. Grooves in a column of the Jefferson Memorial, Washington, D.C., mimic the dark inclusion pattern in the Shelburne Marble and may indicate preferential weathering of inclusions or weathering along inclusion-matrix boundaries in the marble. The column is approximately 3 ft in diameter.

preferentially to the fossil fragments. The matrix calcite fills the spaces between the fossil fragments, the same areas that form the connected pore space. In addition to providing easy access for water, the pore space in the limestone also provides places where salts can precipitate within the stone (Ross and others, 1989). The pressure of growing salts and the pressure from alternate freezing and thawing of ice in cracks may lead to the spalling of portions of stone from buildings (Lewin, 1982; Amoroso and Fassina, 1983).

SUMMARY

The Salem Limestone and the Shelburne Marble are representative of limestones and marbles commonly used in buildings and monuments. Both stones are composed predominantly of calcite. The Salem Limestone is homogeneous in composition and mineralogic characteristics throughout the test block. The Shelburne Marble has compositionally homogeneous mineral phases, but the distribution of those phases within the test block is random. The mineralogy and physical characteristics of the Shelburne Marble and Salem Limestone test blocks described in this study provide a baseline for future studies of the weathering behavior of these stones. It is particularly important to note that the two test stones that were chosen are relatively homogeneous in their characteristics, so that changes that are found in the stones after their exposure at the test sites can be attributed to their exposure experiences and not to individual differences in the samples. Because the Shelburne Marble and the Salem Limestone are representative of typical commercial marbles and limestones, they are likely to be useful in a consortium study of the effects of acid precipitation on these two types of building stones.

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